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GRAIN SIZE DEPENDENT VACANCY SUPERSATURATION PROFILES AND THEIR INFLUENCE ON VOID FORMATION IN AN AUSTENITIC STAINLESS STEEL DURING 1 MeV ELECTRON IRRADIATION

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The computations show that the level of vacancy supersaturation achieved in a grain decreases with decreasing grain size. The grain size dependence of the maximum vacancy supersaturation in the centre of the grains is found to be very similar to the grain size dependence of the maximum void number density and void volume swelling measured in the central regions of the grains. This agreement reinforces the interpretation that the grain size effect is due primarily to the depletion of point defects from the grain interior. It is suggested that the void nucleation is strongly dependent on the level of vacancy supersaturation.

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ABSTRACT

In order to study the effect of grain size on void formation during high energy electron irradiations, the steady-state point defect concentration and vacancy supersaturation profiles have been calculated for three-dimensional spherical grains up to three microns in size. In the calculations of vacancy supersaturation as a function of grain size, the effects of internal sink density and the dislocation preference for interstitial attraction have been included.

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1. INTRODUCTION

It is well established that structural parameters such as dislocations, grain boundaries and precipitates play an important role in determining the swelling behaviour of metals and alloys (Pugh, Loretto and Norris 1971, Corbett and Ianniello 1971, Norris 1972). The influence of grain size on the void nucleation and void volume swelling has been recently studied by one of the present authors (Singh 1973a-c), using 1 MeV High Voltage Electron Microscope. The grain size effect has been explained in terms of a defect depletion model (Singh 1973c) based on the fact that grain boundaries act as neutral and unsaturable sinks for vacancies as well as self-interstitials produced during irradiation. In the model it was assumed that a vacancy concentration profile existing in the denuded zone did not reach its maximum at the end of the void denuded zone but extended into the grain interior. Hence it was suggested that the maximum level of vacancy supersaturation reached in the grain interior of grains smaller than about 2.5 μm decreases with grain size.

The above-mentioned suggestion has been studied by computing the steady state point defect concentration and supersaturation profiles for three-dimensional spherical grains of various sizes; this is described and discussed in the present paper. The profiles have been determined using a computational technique very similar to the one described recently by Foreman (1972). In addition to calculating the diffusional flow of point defects to the grain boundaries, the present calculations also take into account the diffusion of point defects to both the neutral and biased sinks in the material. Similar calculations have also been completed for one dimensional case to determine the effects of foil surfaces (Foreman, to be published).

It is found that in grains smaller than 2.5 μm, the maximum level of vacancy supersaturation decreases by decreasing the size of the spherical grains; the decrease is significant in the grains smaller than one micron.

The correlation between this and the experimental results on the grain size dependent void concentration and void volume swelling is considered. The effect of grain size dependent vacancy supersaturation on void formation is also discussed.

2. FORMULATION OF THE PROBLEM

In order to test the defect depletion model (Singh 1973 c) we need to estimate the loss of vacancies from the grain interior to grain boundaries in grains of different sizes. We propose to do this by calculating the vacancy concentration and supersaturation in the interior regions of three-dimensional grains up to three microns in size. In our calculations the trapping of vacancies and interstitial atoms at the various sinks in the material (voids, dislocations, etc.) is represented by means of a continuum sink, which, following Dienes and Damask (1958), is given by a trapping probability comparable with that of the actual discrete sinks.*) The strength of the equivalent continuum sink is divided into two components: (i) the sink strength α_{void} of the voids and any other neutral sinks, and (ii) the sink strength α_{disl} of the dislocations, which are slightly biased by a preference p towards trapping interstitial atoms. Thus the computations fully take into account the diffusion of the point defects to both the neutral and biased sinks in the material, in addition to calculating in detail the diffusional flow to the grain boundaries.

For the sake of mathematical simplicity the shape of the three-dimensional grains is assumed to be spherical. While making this assumption, we are fully aware of the fact that in thin foil experiments when the grain diameter $d_g \approx$ foil thickness, the grains are intersected by the foil surfaces. Since the grain boundaries and foil surfaces are very similar in nature and strength

*) The use of a continuum sink should be a very good approximation for the dislocations, because they are in a state of continual movement during the irradiation, but it is probably rather less precise for the voids.

as sinks for point defects*), the foil surfaces intersecting the grains of $d_g \approx$ foil thickness can be considered as parts of grain boundaries surrounding the three-dimensional grains. Thus the net effect of the intersections of grains with foil surfaces is to modify the grain geometry from spherical (assumed) to, to a first approximation, rectangular parallelopiped. Consequently, the external sink density (i.e. the trapping power of the grains) would be slightly different in the experimental grains with rectangular parallelopiped geometry than in the spherical grains assumed in our calculation. However, a simple calculation of external sink densities for spherical and rectangular parallelopiped grains of different sizes (Damask and Dienes 1963) would immediately show that for actually used foil thicknesses of 0.5 and 0.8 μm, the external sink densities for both geometries are very similar for grains up to 1.0 and 1.5 μm in size. It must be emphasized here that this is precisely the size range where the grain size effect is most marked. The external sink density for grains larger than that quoted above would be somewhat greater in the case of geometry actually used than the one assumed in our calculations. However, the effect of this difference on the correlation between the calculated and experimental results is thought to be insignificant (see discussion).

Since the observed grain size effect is thought to be nucleation controlled (Singh 1973c), we shall calculate the vacancy concentration and supersaturation particularly relevant to early stages of void formation. The void sink density during this stage is comparable with the dislocation sink density and therefore we shall use the measured dislocation sink density in our calculations (see discussion).

*) The thicknesses of the denuded zones along grain boundaries and foil surfaces are found to be very similar (Singh, unpublished work).

3. CALCULATION OF VACANCY CONCENTRATION AND SUPERSATURATION PROFILES

The steady state diffusion equations for the irradiation - produced vacancies and interstitial atoms, including the effect of direct recombination, are

$$K + D_v \nabla^2 v - [\alpha_{void} + \alpha_{disl}] v D_v - Z \nu_i i v = 0 \quad (1)$$

$$K + D_i \nabla^2 i - [\alpha_{void} + (1+p)\alpha_{disl}] i D_i - Z \nu_i i v = 0 \quad (2)$$

where K is the defect production rate (dpa per unit time), D_v and D_i are the vacancy and interstitial atom diffusion coefficients respectively, v and i are their respective fractional concentrations, Z is a numerical factor determined by the number of sites around a vacancy at which an interstitial atom will directly recombine ($Z \simeq 10$), and ν_i is the jump frequency of an interstitial atom. Since we have assumed the grains to be spherical, $\nabla^2 = d^2/dr^2 + (2/r)d/dr$ and the diffusion problem becomes spherically symmetric. The boundary conditions are $i = v = 0$ at $r = \frac{1}{2}d_g$, where d_g is the grain diameter, since the grain boundary is believed to be a perfect (unbiased) sink for both the interstitial atoms and vacancies.

We shall define the vacancy supersaturation S to be

$$S = vD_v - iD_i \quad (3)$$

since it is this quantity that determines the rate of growth of a void. Thus from equs. (1) and (2) S is given by

$$\nabla^2 S - \alpha S + \alpha_{disl} p(V - S) = 0 \quad (4)$$

$$K + \nabla^2 V - \alpha V - \frac{Z\nu_i}{D_v D_i} V (V - S) = 0 \quad (5)$$

where $\alpha = \alpha_{void} + \alpha_{disl}$. ..... (6)

is the total sink strength and

$$V = vD_v \quad (7)$$

is a measure of the flux of vacancies being trapped at a sink of unit strength.

Equations (4) and (5) can readily be solved numerically by an iterative procedure, but this is unnecessary in the present application because we can make use of the fact that the dislocation preference is small ($p \sim 1\%$) and we can therefore use first order perturbation theory. Accordingly we make a Taylor series expansion of V and S in powers of p

$$V = V^{(0)} + pV^{(1)} + p^2 V^{(2)} + \ldots\ldots \quad (8)$$

$$S = pS^{(1)} + p^2 S^{(2)} + \ldots\ldots \quad (9)$$

where the $S^{(0)}$ term in eq. (9) has been omitted because the vacancy supersaturation is zero in the absence of any biased sinks, i.e. $vD_v = iD_i$ when $p = 0$. Substituting these expansions into the differential equations (4) and (5) and equating powers of p gives

$$\nabla^2 S^{(1)} - \alpha S^{(1)} + \alpha_{disl} V^{(0)} = 0 \quad (10)$$

$$K + \nabla^2 V^{(0)} - \alpha V^{(0)} - \frac{Z\nu_i}{D_i D_v} V^{(0)2} = 0 \quad (11)$$

for the lowest order terms $V^{(0)}$ and $S^{(1)}$. Equation (11) is the normal diffusion equation for determining the concentration profile across the grain. This can readily be solved numerically in much the same way as for the one-dimensional case of a thin foil (Foreman 1972). Then having determined $V^{(0)}$ in this way eq. (10) may be integrated numerically to give the vacancy supersaturation $S = pS^{(1)}$.

For computational purposes it is convenient if we (a) minimize the number of adjustable parameters in the calculation, and (b) normalize the vacancy concentration and supersaturation profiles to their values in the absence of diffusion to the grain boundaries. If we denote the normalized values of V and S by V' and S' then on setting $\Psi = V/Kd_g^2$ the differential equations for V' and S' may be shown to be

$$\nabla^2 S' - \alpha d_g^2 (S' - V') = 0 \qquad (12)$$

in which V' is given by

$$1 + \nabla^2 \Psi - \alpha d_g^2 \Psi - f \Psi^2 = 0 \qquad (13)$$

where

$$f = \frac{Z \nu_i K d_g^4}{D_v D_i} \qquad (14)$$

$$V' = \Psi / \Psi_o \qquad (15)$$

and Ψ_o is the value of Ψ without the diffusion term, i.e.

$$1 - \alpha d_g^2 \Psi_o - f \Psi_o^2 = 0 \qquad (16)$$

All distances occuring in the ∇^2 diffusion terms are now in units of the grain diameter d_g, since we require to determine the profile relative to the grain size.

It will be noted from equations (12) to (16) that the normalized results depend on the values of the two non-dimensional quantities f and αd_g^2, both of which have a simple physical interpretation. It may readily be shown that $f^{-1/4}$ is the mean free path of a vacancy before it is annihilated by a diffusing interstitial atom (in the absence of sinks) whilst $(\alpha d_g^2)^{-1/2}$ is the mean free path of a vacancy before being trapped at a sink (in the absence of grain boundaries and direct recombination), both numbers being in units of the grain diameter d_g.

Equations (12) to (16) also show that the shapes of the normalized profiles depend only on the total sink strength α and are unaffected by the way in which this is divided between α_{void} and α_{disl}. The normalized profiles are also independent of the precise value of the dislocation preference p because on the basis of first order perturbation theory both S and

its normal value are proportional to p, so that p cancels when deriving the normalized profile S'. These simplifications would disappear if higher order terms were taken into account, but in view of the smallness of the dislocation preference ($p \sim 1\%$) the errors involved in neglecting the higher order corrections should themselves be ~1%, which is an entirely acceptable level of accuracy for this type of calculation.

On the basis of the procedure outlined above, the vacancy concentration (C/C_o) profiles are calculated as a function of parameters f and αd_g^2 and are shown in fig. 1. It is worth noting that the vacancy concentration at $f \geq 10^4$ is no longer influenced by αd_g^2 in the range $0 \leq \alpha d_g^2 \leq 40$ studied, and that $(C/C_o) = 1$ at $f \geq 10^5$ for $\alpha d_g^2 \geq 0$. The vacancy supersaturation (S/S_o) profiles have also been calculated as a function of f and $(\alpha d_g^2)^2$ for f and $(\alpha d_g^2)^2$ in the range of $1 \leq f \leq 10^7$ and $10 \leq (\alpha d_g^2)^2 \leq 10^7$, respectively. We find that the supersaturation level increases with increasing f and $(\alpha d_g^2)^2$ and approaches the bulk value (i.e. $S/S_o=1$) at $(\alpha d_g^2)^2=10^5$ for all values of f. Furthermore, the supersaturation level for a given value of $(\alpha d_g^2)^2$ becomes insensitive to any further increase in f at $f \geq 10^5$. An example of the vacancy supersaturation profiles as a function of $(\alpha d_g^2)^2$ and at $f=10^6$ is shown in fig. 2. Finally, we calculate f and $(\alpha d_g^2)^2$ values for our stainless steel under 1 MeV electron irradiation at 600°C as a function of grain size d_g, using the same d_g for both f and $(\alpha d_g^2)^2$. In calculations of f and $(\alpha d_g^2)^2$ we use $Z = 10$, $K = 5.16 \times 10^{-3}$ dpa sec^{-1}, $\nu_i = D_i/\lambda^2 \nu_i = 1$ where $\lambda = 2.52$ Å (point defect jump distance for iron), $D_v = 0.6 \exp(-1.4/kT)$ cm^2/sec, and α_{disl} (measured for our stainless steel during irradiation at 600°C) $= 5 \times 10^9$ cm/cm^3. Since the observed variation in dislocation density with grain size is almost negligible, in our calculation we use $\alpha_{disl} = 5 \times 10^9$ cm/cm^3 for all grain sizes in the range 0.5 to 3.0 μm. We then compute the vacancy supersaturation profiles as a function of grain size, d_g; this is shown in fig. 3.

The results quoted above do not take account of the presence of a void denuded zone along the grain boundaries. However, we have repeated the calculations to check the effect of void denuded zone on the supersaturation

profiles, using the observed void denuded zone width of 0.03 μm (Singh 1973 d) in 0.5 μm and 2.0 μm dia. grains. We find that in both cases there is no noticeable effect of the void denuded zones on supersaturation profiles.

4. EFFECT OF GRAIN SIZE ON VACANCY SUPERSATURATION AND VOID FORMATION

The effect of grain size on the vacancy supersaturation profiles within the grains is quite apparent from fig. 3. The fact that the vacancy supersaturation level in 2.50 μm grain (at $r'd_g = 0$) approaches its bulk value, would suggest that in grains with $d_g \geq 2.50$ μm the effect of grain size on void formation and growth (through vacancy depletion from the grain interior) should be negligible. The above prediction is borne out by our experimental results which show that the void volume swelling ($\Delta V/V$) in 2.60 μm (without helium) and 2.77 μm (with 10 ppm helium) grains is much the same as in type 316 stainless steel with $d_g \simeq 50$ μm (Singh 1973 c, figs. 7 and 8).

The maximum value of vacancy supersaturation in the centre of all the grains mentioned in fig. 3 is plotted against grain size in fig. 4. Fig. 4 also includes the maximum void number density and void volume swelling ($\Delta V/V$) measured in the centre of the grains of various sizes: the foil thicknesses used were about 0.5 μm (open symbols) and 0.8 μm (closed symbols). These results clearly demonstrate that the experimentally measured dependences of the maximum void number density and the void volume swelling on grain size are very similar to that of the calculated vacancy supersaturation on grain size in the whole grain-size-range investigated.

5. DISCUSSION

The correlation between the grain size dependence of vacancy supersaturation and the maximum void number density and the void volume swelling (fig. 4) reinforces the earlier suggestion (Singh 1973 c) that the grain size effect is due primarily to the depletion of vacancies from the

grain interior which, in turn, suppresses the vacancy supersaturation level. One of the important consequences of the suppression of vacancy supersaturation by decreasing grain size (fig. 3) is a substantial decrease in the void number density (fig. 4). This clearly indicates that the nucleation of voids is strongly dependent on the level of vacancy supersaturation. However, the mechanism for the dominant effect of supersaturation on the void number density, observed in our experiments, is not understood in detail although the effect seems to be quite reasonable. The problem of the nucleation mechanism is being considered the details of which are clearly beyond the scope of the present paper.

The effect of vacancy supersaturation on the void volume swelling can be further discussed in terms of its effect on void growth rate. From steady state diffusion theory Greenwood, Foreman and Rimmer (1959) have shown that, neglecting the effect of thermal vacancies, the growth rate of a small spherical void is proportional to the vacancy supersaturation S[*]. The void growth rate is therefore expected to decrease with decreasing vacancy supersaturation, i.e. with decreasing grain size. Experimentally, we do indeed observe that the growth rate is generally lower in smaller grains (Singh 1973 d). However the effect of grain size on the void growth rate is not as strong as expected from its effect on $(S/S_o)_{max}$. This arises because of the fact that the void sink density, during the growth period, is comparable to the dislocation sink density in grains smaller than about 1.0 μm, which is the condition for the optimum void growth. As the grain size increases, the effect of the enhanced supersaturation (fig. 4) on the void

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[*] This can be used as a basis for comparison of the growth rates of voids in our grains of different sizes, particularly at low doses where the defect denuded zones around the voids are expected to be reasonably well separated (see Foreman 1970)

growth is compensated by the increase in the void sink density beyond the optimum. Thus we see that the unexpectedly small effect of supersaturation on the void growth can be readily understood.

It is also worth mentioning that the reason why the grain size effect persists up to a grain size of about 2.5 μm (figs. 3 and 4) is NOT because vacancies are affected more by grain boundaries than foil surfaces but because of a geometrical factor arising from the three-dimensional coverage of grains with grain boundaries and/or foil surfaces. The introduction of grain boundaries modifies the three-dimensional distribution and density of external sinks such that the overall defect trapping power of grain boundaries increases with decreasing grain size. The reason why the above explanation of the grain size dependent vacancy depletion from the grain interior is very unlikely to be applicable to a similar depletion of helium atoms has already been discussed in terms of trapping of helium atoms at vacancy clusters (Singh 1973 c). Finally whether or not the observed grain size effect would be modified by (a) the presence of solid impurity atoms (i.e. carbon) within the grains and/or at the grain boundaries, and (b) the structure of grain boundaries themselves, cannot, at present, be predicted with much accuracy because very little is known about the effect of these parameters on defect accumulation during irradiation.

6. CONCLUSIONS

Vacancy concentration and supersaturation profiles within grains of different sizes have been computed. In these calculations the effects of internal sink density and dislocation bias for interstitial attraction have been included. It is found that the maximum level of the vacancy supersaturation in the centre of the grains increases with increasing grain size up to $d_g = 2.5$ μm; this is in qualitative agreement with the experimentally measured grain size dependent void number density and void volume swelling.

The above mentioned agreement reinforces the suggestion that the grain size effect is due mainly to the defect depletion from the grain interior (Singh 1973 c). The present work also supports the view that the void nucleation is strongly influenced by the level of vacancy supersaturation.

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REFERENCES

CORBETT, J. W., and IANNIELLO, L. C., Eds., 1971, Radiation Induced Voids in Metals, Proc. Int. Conf., Albany.

DAMASK, A. C., and DIENES, G. J., 1963, Point Defects in Metals, Gordon and Breach, New York, p. 79 - 81.

DIENES, G. J., and DAMASK, A. C., 1958, J. Appl. Phys., 29, 1713.

FOREMAN, A. J. E., 1970, AERE-R-6358.

FOREMAN, A. J. E., 1972, Radiation Effects, 14, 175.

GREENWOOD, G. W., FOREMAN, A. J. E., and RIMMER, D. E., 1959, J. Nucl. Mat., 4, 305.

NORRIS, D. I. R., 1972, Radiation Effects, 14, 1; 15, 1.

PUGH, S. F., LORETTO, M. H., and NORRIS, D. I. R., Eds., 1971, Voids Formed by Irradiation of Reactor Materials, Proc. BNES European Conf. Reading.

SINGH, B. N., 1973 a, J. Nucl. Mat., 46, 99.

1973 b, Nature Physical Science, 224, 142.

1973 c, Phil. Mag., in press.

1973 d, Risø Rept. No. 287.

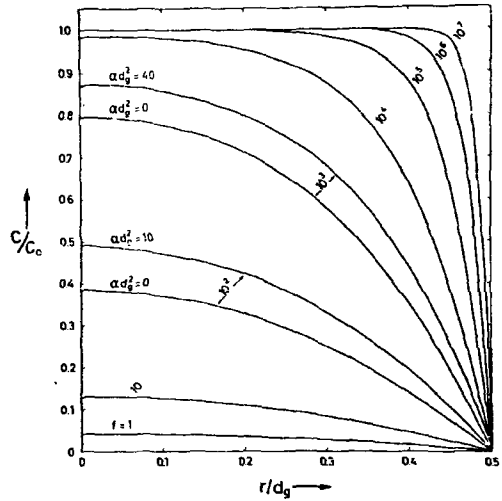

Fig. 1. Steady-state concentration profiles of irradiation induced point defects in spherical grains with $f = 1, 10, \ldots 10^7$ and $\alpha d_g^2 = 0, 10, 40$. The profiles for $f \geq 10^4$ remain the same for $\alpha d_g^2 = 0$, 10 and 40. The concentration C/C_o is the defect concentration relative to a very large grain and $r/d_g = 0$ is the centre of the grain. The dependence of the profiles on grain size, dose rate, temperature, and material is contained in the value of the parameter f; the internal sink density is represented by αd_g^2.

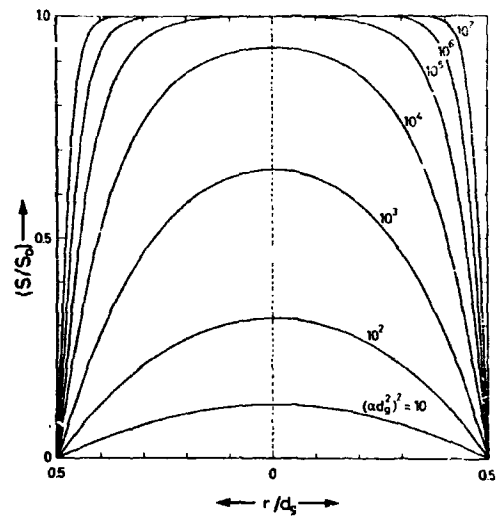

Fig. 2. Steady-state vacancy supersaturation profiles for spherical grains with $(\alpha d_g^2)^2 = 10, 10^2 \ldots 10^7$ at $f = 10^6$. The supersaturation (S/S_o) is the vacancy supersaturation relative to a very large grain. The profiles with different $(\alpha d_g^2)^2$ values do not change for $f \geq 10^5$ (see text).

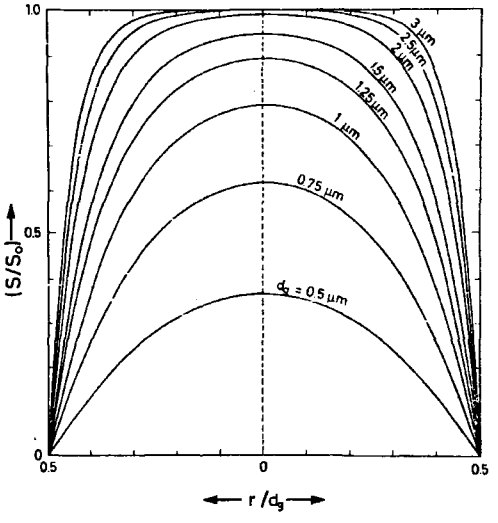

Fig. 3. Vacancy supersaturation profiles calculated for different grain sizes; here f and $(\alpha d_g^2)^2$ are calculated for our material under electron irradiation at 600°C (see text).

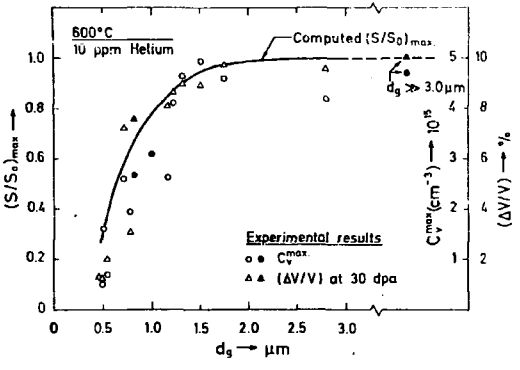

Fig. 4. Variation of $(S/S_o)_{max}$, C_v^{max}, and $(\Delta V/V)$ at 30 dpa with grain size; $(S/S_o)_{max}$ is the value of (S/S_o) at $r/d_g=0$ in fig. 3, C_v^{max} and $(\Delta V/V)$ are measured values of void number density and void volume swelling, respectively, in the centre of the grain (material description and experimental procedure are given in Singh 1973c). Open and closed symbols refer to foil thicknesses of about 0.5 µm and 0.8 µm, respectively.